Toxicity of PVC Cable Compounds During Combustion Compared to Halogen-Free Alternatives

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4TH PVC4CABLES CONFERENCE

16 OCTOBER IN PRAGUE

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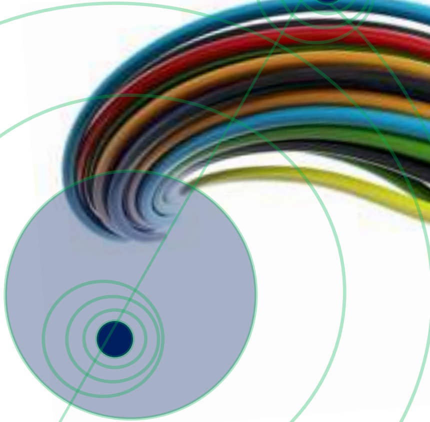
1 Introduction

The paper addresses **common misconceptions** about PVC cables, particularly those surrounding **the role of HCl in fire safety** and the presence of more **toxic fumes** during the combustion in comparison to Halogen Free Flame-Retardant (HFFR) cables. Those misconceptions are often utilized in the brochures of our competitor plastics to remark the lower toxicity of HFFR alternatives and inside technical committees to give a priori exclusion of PVC in specific application often without any scientific basis. [1,2,3]

Construction Product Directive (CPD) [4] and Construction Product Regulation (**CPR**) [5] contributed to this witch hunt with the **introduction** of additional **classification for acidity only for cables**, where acidity assessment is seen as fundamental parameter in fire safety. Most of the fire scientists consider acidity as a secondary parameter, while **heat release rate** is the "**single most important variable in fire safety."** [6,7] Smoke is another critical parameter, while toxicity before and after flashover is ruled by mainly by CO. [8-12]. In a real fire scenario CO is the big toxic killer in smoke [7] while HCl rarely exceed its LC_{50}. After flashover it is released from every polymer despite its chemical structure for a 20 % of its weight. [7] Before the flashover tenability is mainly driven by CO. [11,12] Therefore, "…there is no relationship whatsoever between acid gases (or acidity of solutions) and smoke toxicity." [7]



1 Introduction

Despite all considerations about the role of acidity in fire safety, the paper presents the performance of advanced PVC compounds for cables developed to reduce smoke and acidic fumes during fires without affecting flame retardance. They are developped by Gruppo Cavi Italia through a research funded by PVC4cables [13-26]. They are called **low smoke acidity** (LSA) **compounds**.

This new compounds were evaluated vs. the HFFR counterparts in terms of effluent emission in thermal decomposition and combustion using as hyphenated technique pyrolysis gas chromatography mass spectrometry (**PY-GC/MS**) and **toxicity index** according to CEI 20-37/4-0 [27]. Both are based on a bench scale test which burns completely the test specimens and does not take in account the quantity of the material in the cable.

Furthermore, an Italian kind of CPR cables FG16OR16 manufactured with LSA PVC compounds was tested vs. the counterpart HFFR FG16OM16, performing the medium scale fire test EN 50399 [28] in terms of flame spread (FS), Fire growth rate (FIGRA), total heat release (THR), peak of HRR and SPR, and total smoke production (TSP).

CO, CO2 and HCl release were also measured, and the toxicity of effluents expressed as fractional effective dose (FED) according to ISO 13344 was calculated. [29]

2 Decomposition / Combustion of PVC and PE

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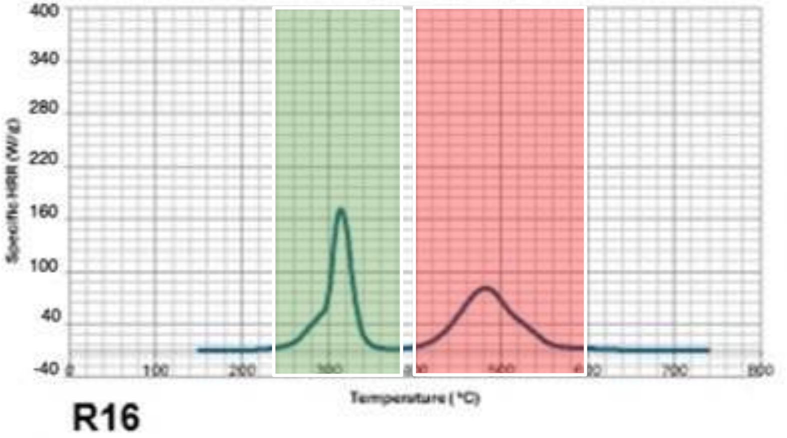
Ref. 30 from Pasquale Lombardo studied the decomposition / combustion at 500 °C and 950°C of a standard R16 PVC compound, R16 LSA and the HFFR counterpart (M16), utilizing PY-GC/MS

Decomposition & combustion PVC [17]



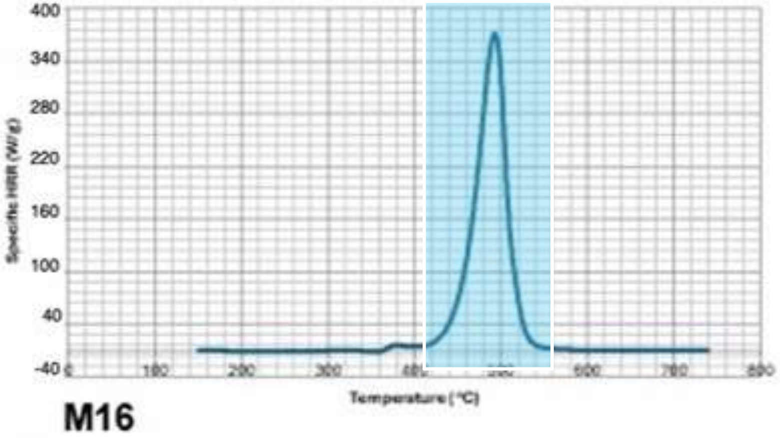
ASTM D 7903 method A [31]

First stage (220-350°C), HCl is released via zip-elimination, forming polyene sequences that can rearrange to release aromatic compounds (i.e. heat release and smoke), and crosslinked matrix. HCl reduces and plasticizer increases the flame.

Second stage (400-600°C), the crosslinked structure releases aliphatic hydrocarbons, which burn with high heat but less smoke. The process concludes with char formation, limiting further heat release and flaming dripping.

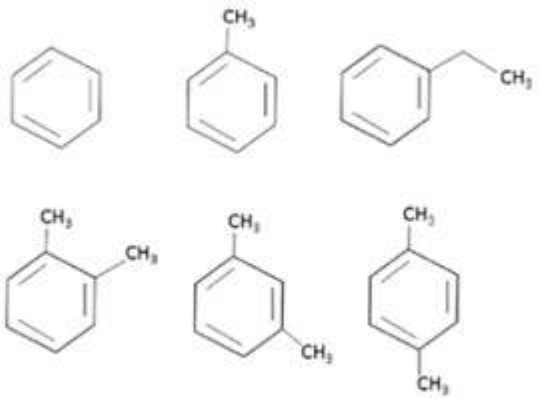
Additives can shape the sHRR (T)

Decomposition & combustion HFFR



400-500°C: Volatilization of Hydrocarbons

The breakdown of the polymer leads to the volatilization of hydrocarbons, releasing gases such as aliphatic and aromatic hydrocarbons, which sustain the flame. As soon as the temperature increase the formation of aromatics is the preferable route [32]



3 Misconceptions

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Withstanding misconceptions on PVC fire behaviour

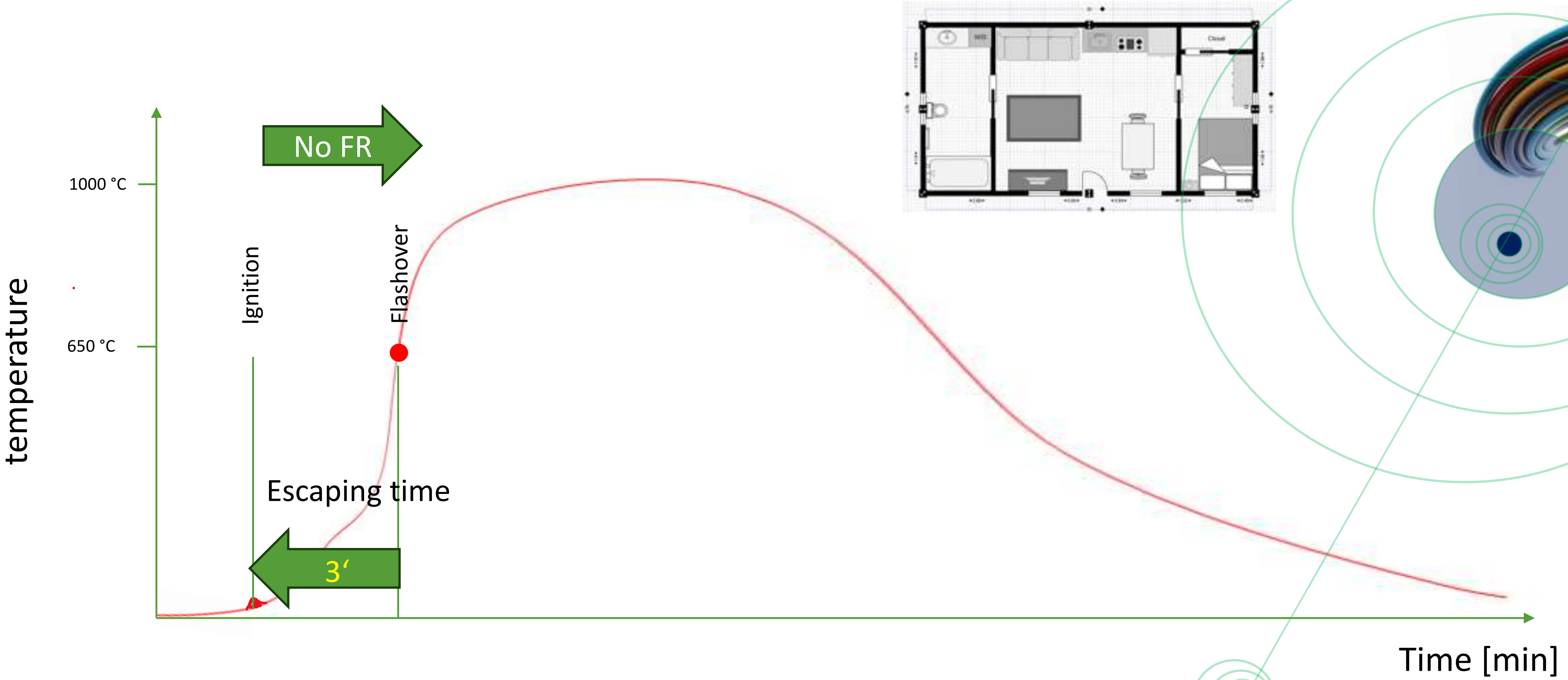
If not → PVC deselection

Smoke production	→	PVC releases black & dense smokes
Smoke toxicity	→	PVC releases more toxic smokes
acidity	→	Acidity is a critical parameter in fire safety

TOPIC

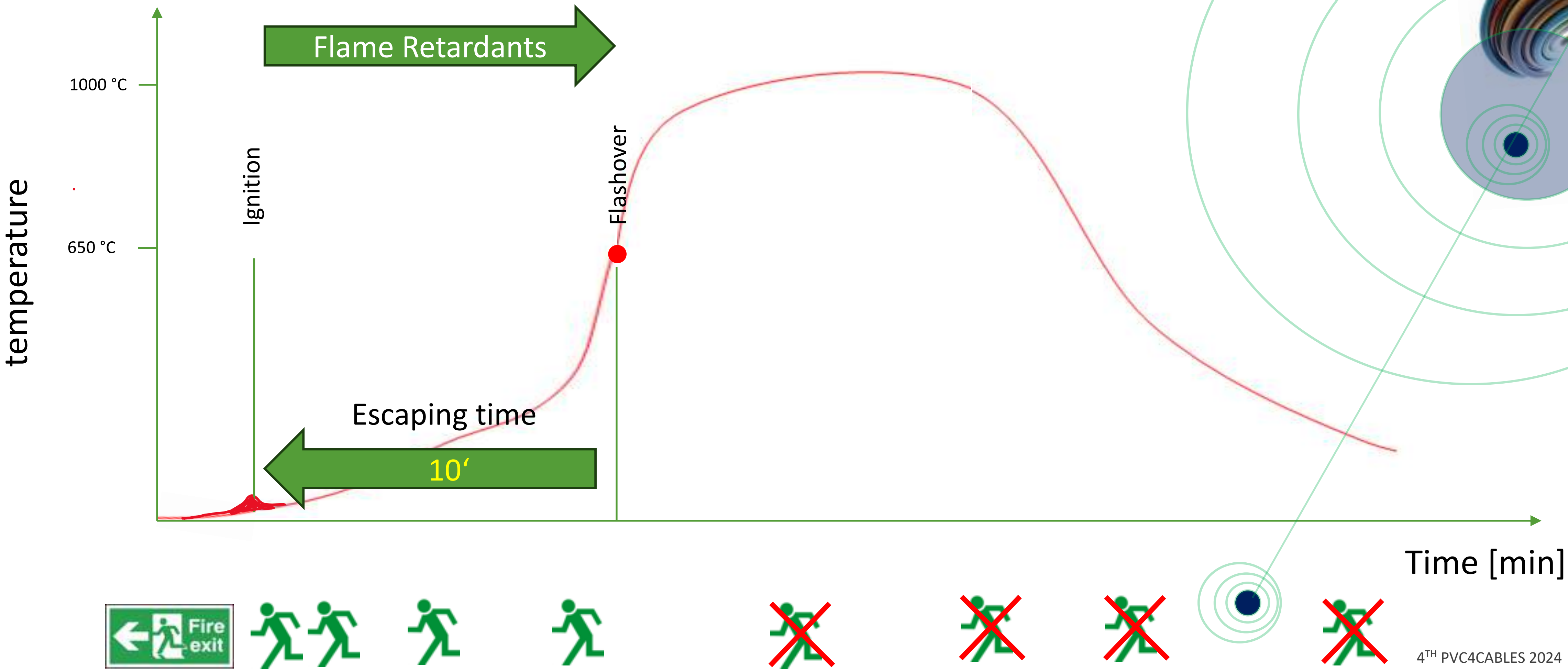
Misconceptions. Fire safety in nutshell

Fire Scenario number 1: **3** minutes between ignition and flashover (the point of non-return)



Misconceptions. Fire safety in nutshell

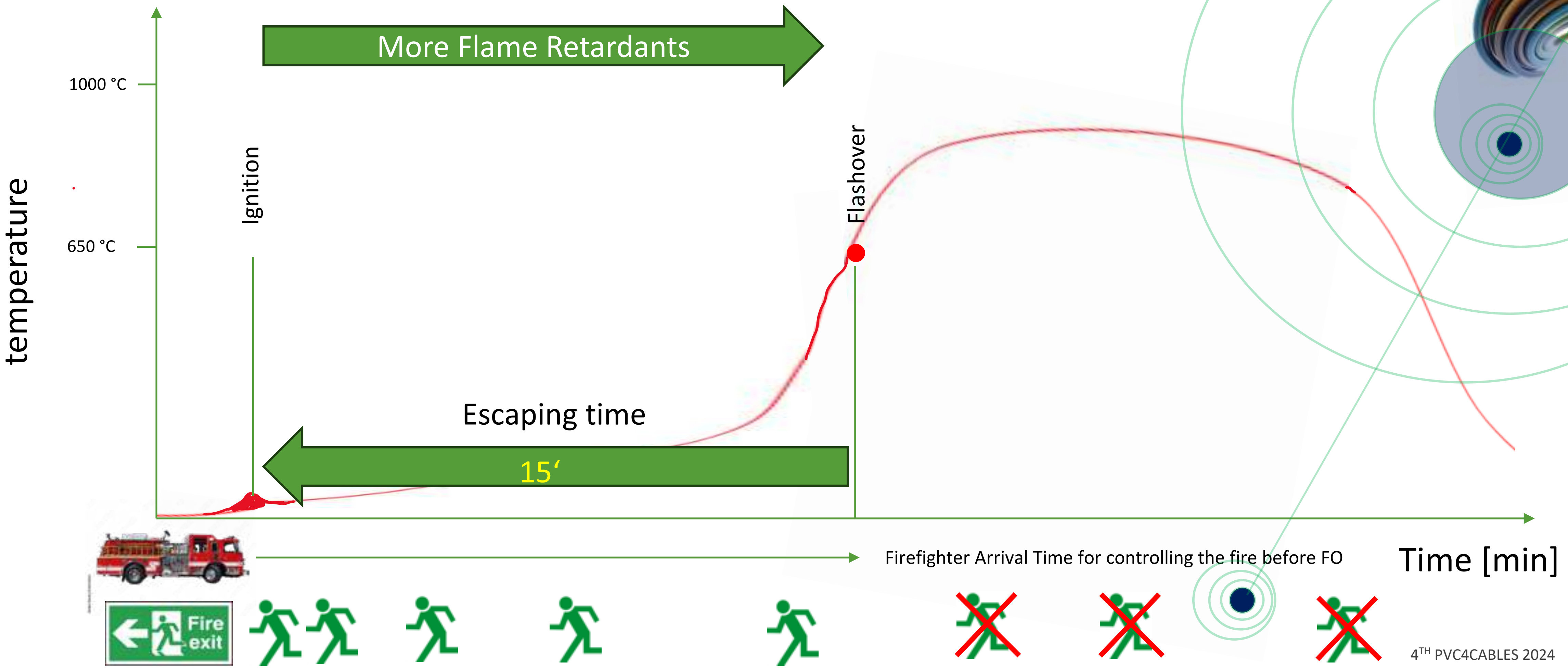
Fire Scenario number 2: **10** minutes between ignition and flashover (the point of non-return)



3 Misconceptions. Fire safety in nutshell

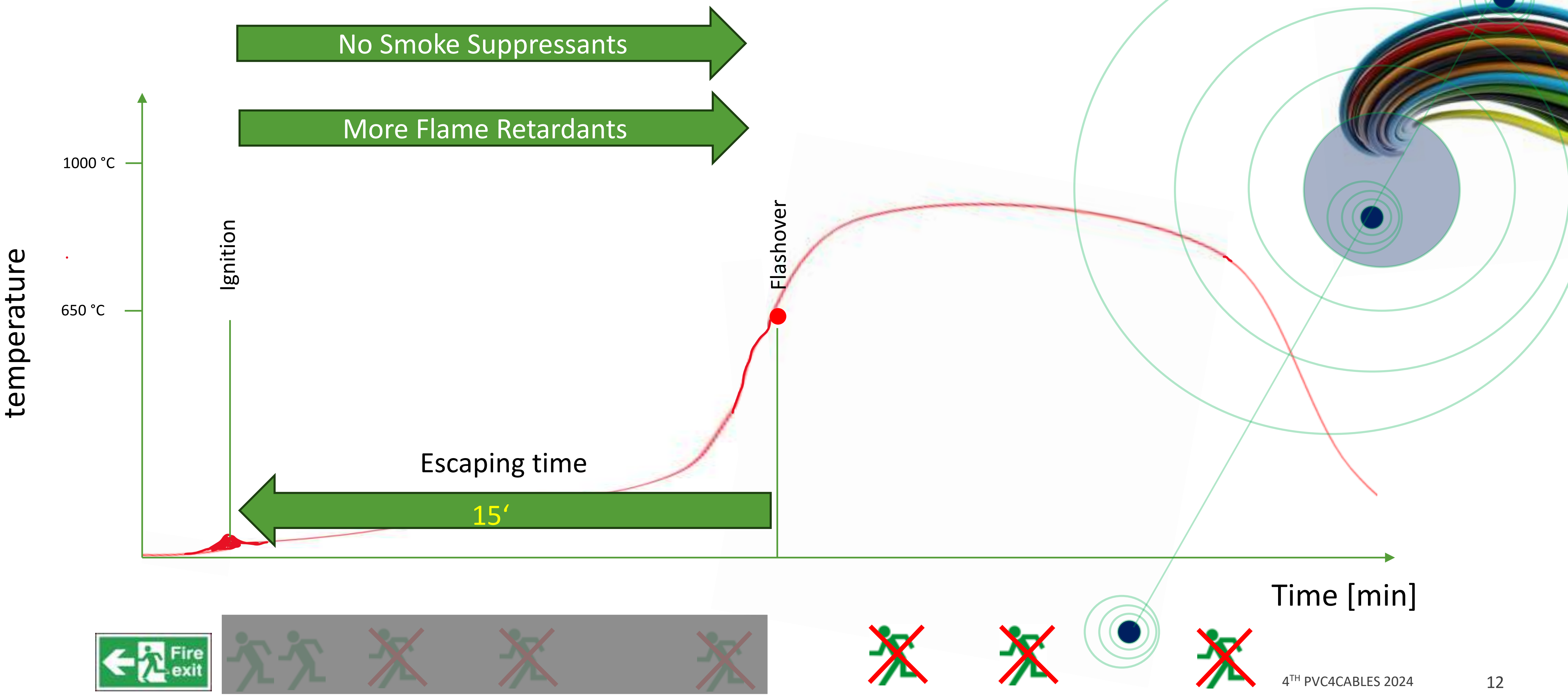
Fire Scenario number 3: 15 minutes between ignition and flashover (the point of non-return)

heat release rate is the "**single most important variable in fire safety" [6]**



Misconceptions. Fire safety in nutshell

Fire Scenario number 4: **15** minutes between ignition and flashover (the point of non-return), dense smoke



Misconceptions. Fire safety in nutshell

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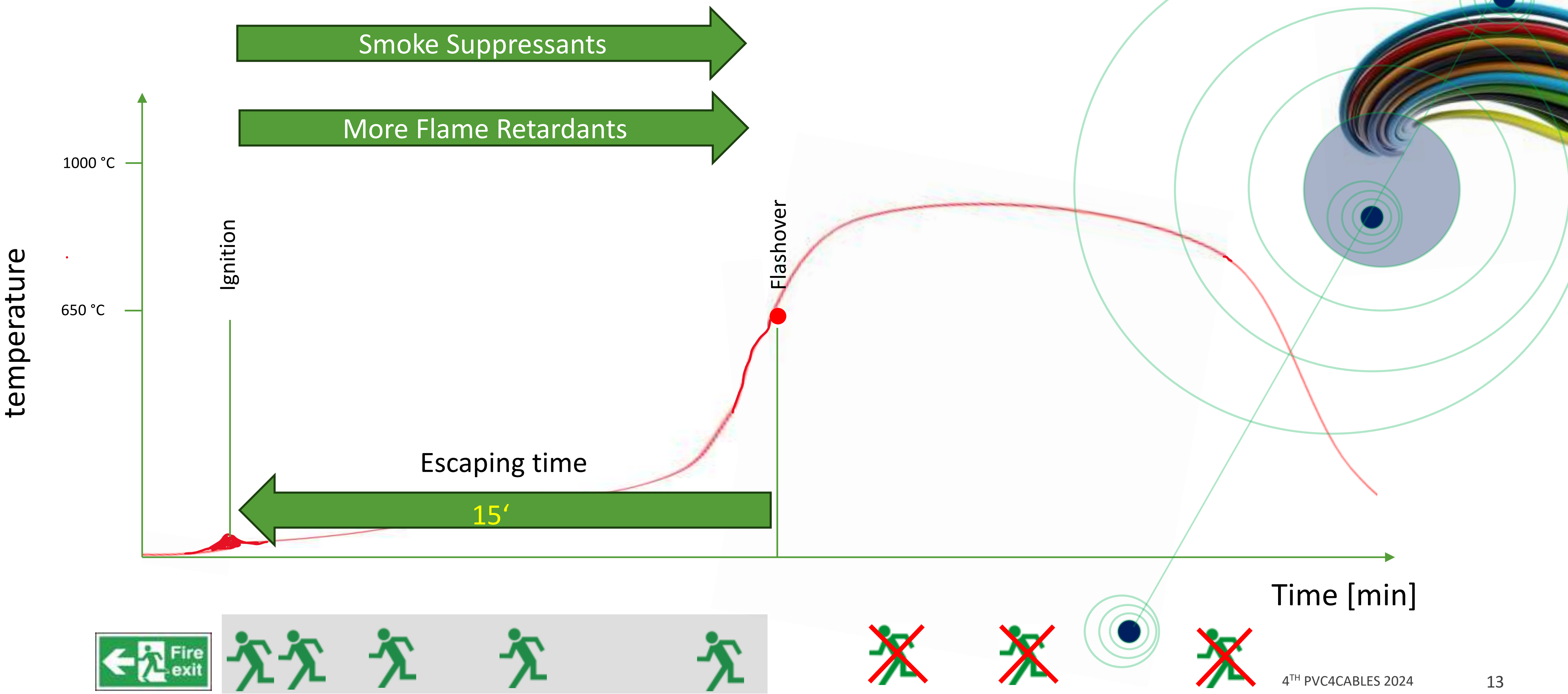
Fire Scenario number 5: 15 minutes between ignition and flashover (the point of non-return), no dense smoke

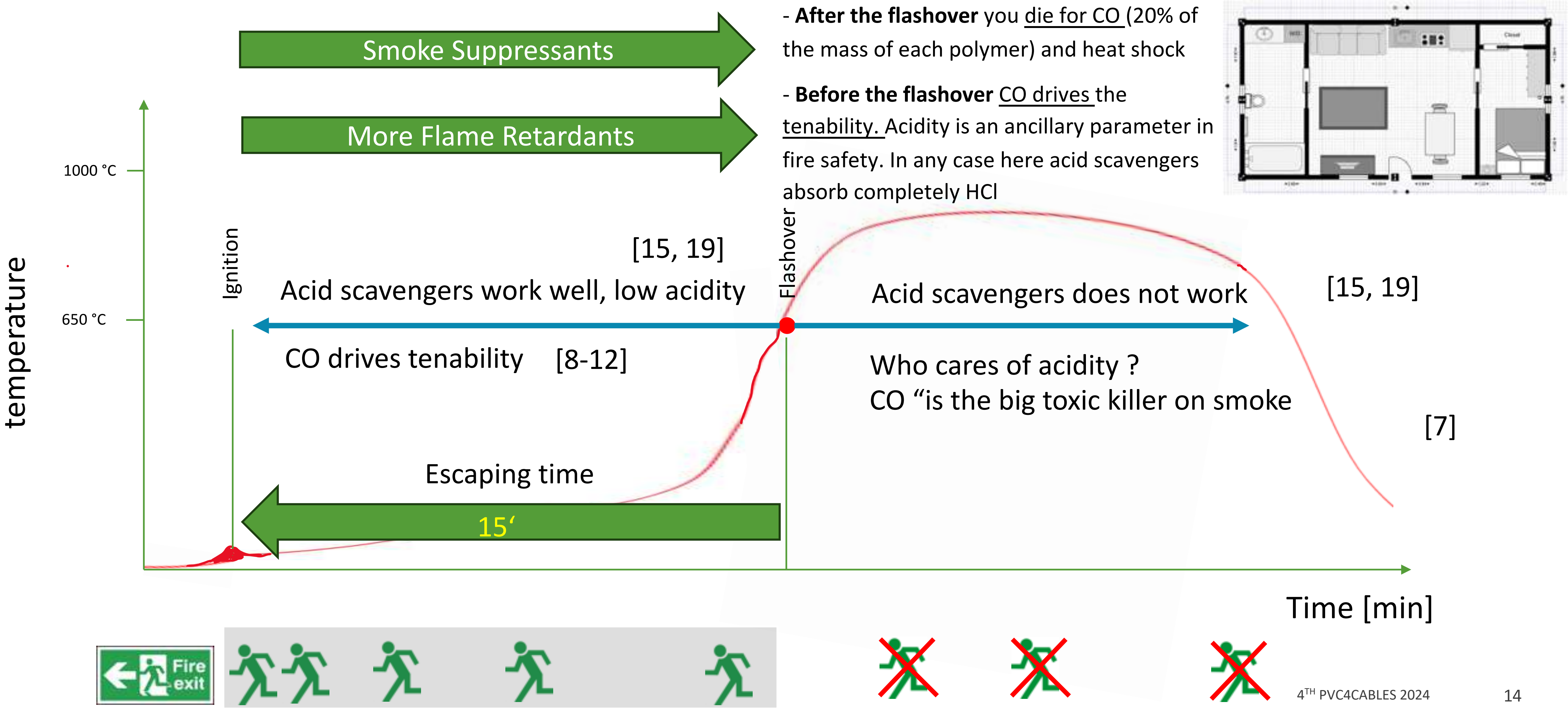


3 Misconceptions. Fire safety in nutshell

PVC 4 CABLES

Fire Scenario number 5: 15 minutes between ignition and flashover (the point of non-return), no dense smoke

- **After the flashover** you die for CO (20% of the mass of each polymer) and heat shock
- **Before the flashover** CO drives the tenability. Acidity is an ancillary parameter in fire safety. In any case here acid scavengers absorb completely HCl



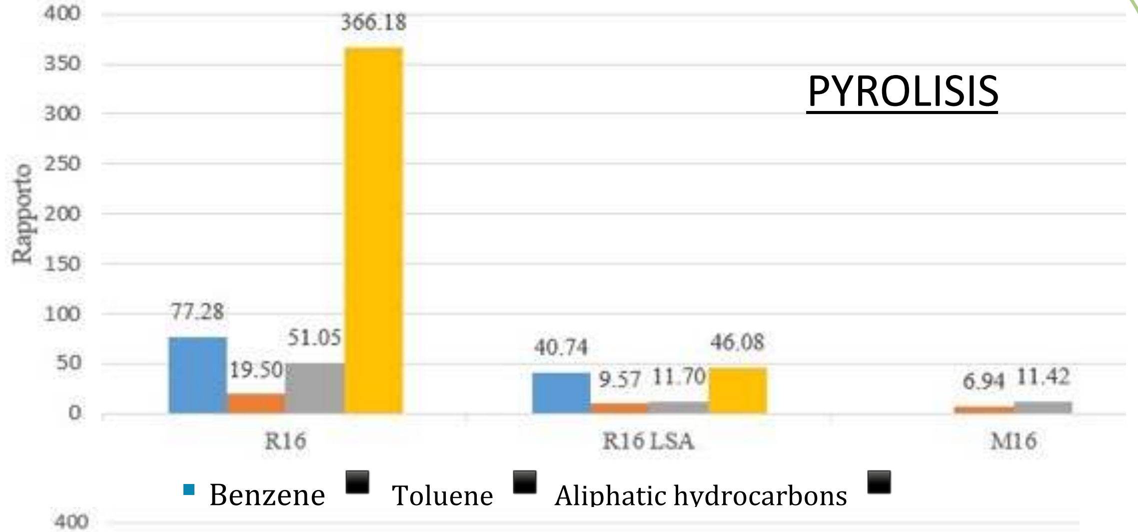
LSA Cables n1 (2024): PY-GC/MS of compounds

PVC4CABLES

Ref. 33 gives the decomposition / combustion at 500 °C and 950°C of a standard R16 PVC compound, R16 LSA and the HFFR counterpart (M16), utilizing PY-GC/MS. Focus on total fuels

Volatile organic effluents released at 500°C

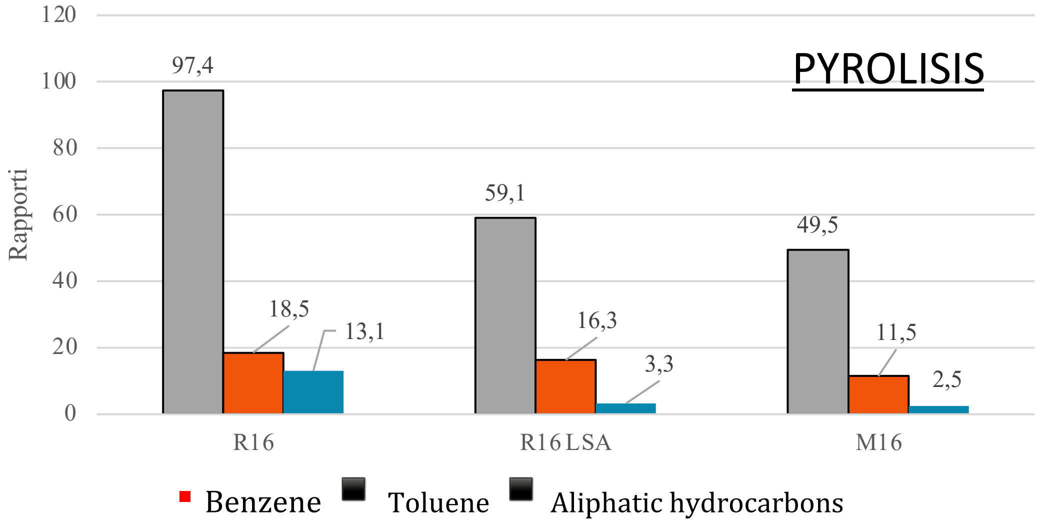
PYROLISIS



COMBUSTION

Volatile organic effluents released at 950°C

PYROLISIS



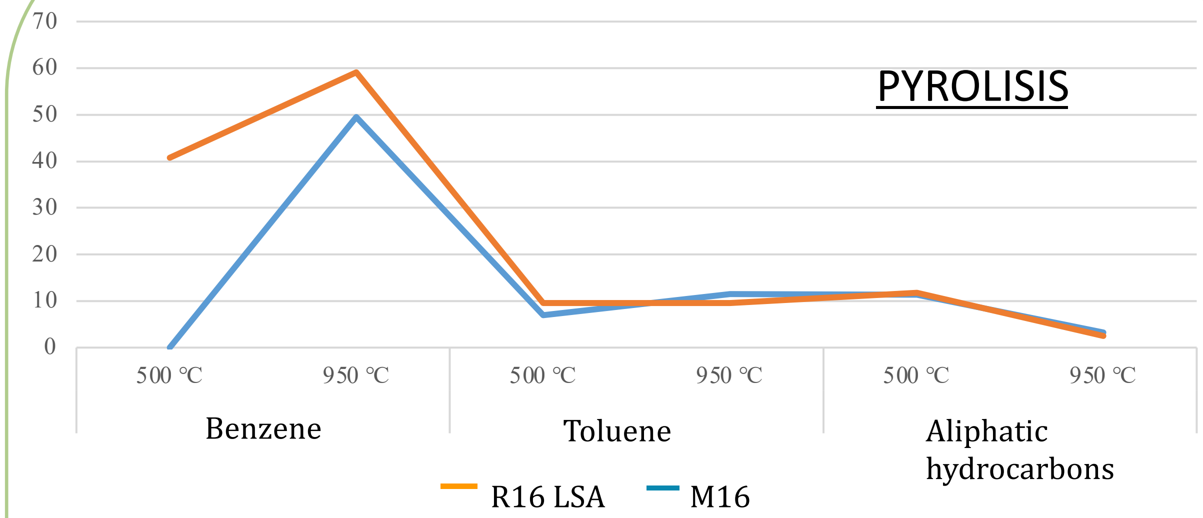
COMBUSTION

No signals, complete combustion

4 LSA Cables n1 (2024): : PY-GC/MS of compounds

Ref. 33 gives the decomposition / combustion at 500 °C and 950°C of a standard R16 PVC compound, R16 LSA and the HFFR counterpart (M16), utilizing PY-GC/MS. Focus on fuels from polymers

Volatile organic effluents in R16 LSA/M16



COMBUSTION

CO, CO_2 and H_2O

4 LSA Cables n1 (2024): CEI 20-37/4-0 of compounds

PVC4CABLES

Ref. 33. evaluated each plastic component of the cables in Table 15.1 according to CEI 20-37/4-0. [27]
It is a small-scale test where 1 g of compounds is totally burnt at 800 °C in a tube furnace with an air flow of 120 l/h for 20 min.

Toxicity Index T is calculated through the following formulation

$$T = C_1/C^\wedge_1 + C_2/C^\wedge_2 + ... + C_i/C^\wedge_i + C_n/ C^\wedge_n$$

Using as reference the toxic potentials of each component.

The method is a lab scale test burning completely the sample and not considering the amount of the material in the cables.

Cable	Diameter	Construction	Sheath Weight (g/m)	Insulation Weight (g/m, each)	Filler Weight (g/m)
Polythene-based cable FG16OM16 SG 1.5 mm² "zero halogen" (Lab ref: 900/24)	12.3 mm	1 sheath, 5 insulations, 1 filler	137.6	4.3	4.1
PVC-based cable FG16OR16 SG 1.5 mm² (Lab ref: 901/24)	12.1 mm	1 sheath, 5 insulations, 1 filler	145.8	4.4	4.3

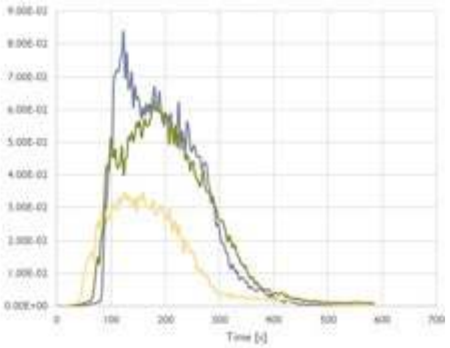
Table 15.1

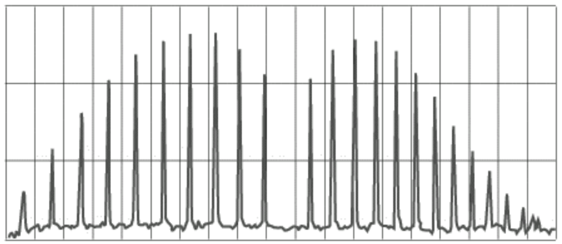
Component	C_CO2 (p.p.m.)	C_CO (p.p.m.)	C_HCl (p.p.m.)	Index T
"Zero halogen" cable Sheath	66364	2532	0	1.30
"Zero halogen" cable Insulation	50734	4453	0	1.62
"Zero halogen" cable Filler	96927	3755	0	1.91
PVC cable Sheath	85313	3580	469	2.69
PVC cable Insulation	50734	3754	0	1.45
PVC cable Filler	111946	5414	1340	5.15

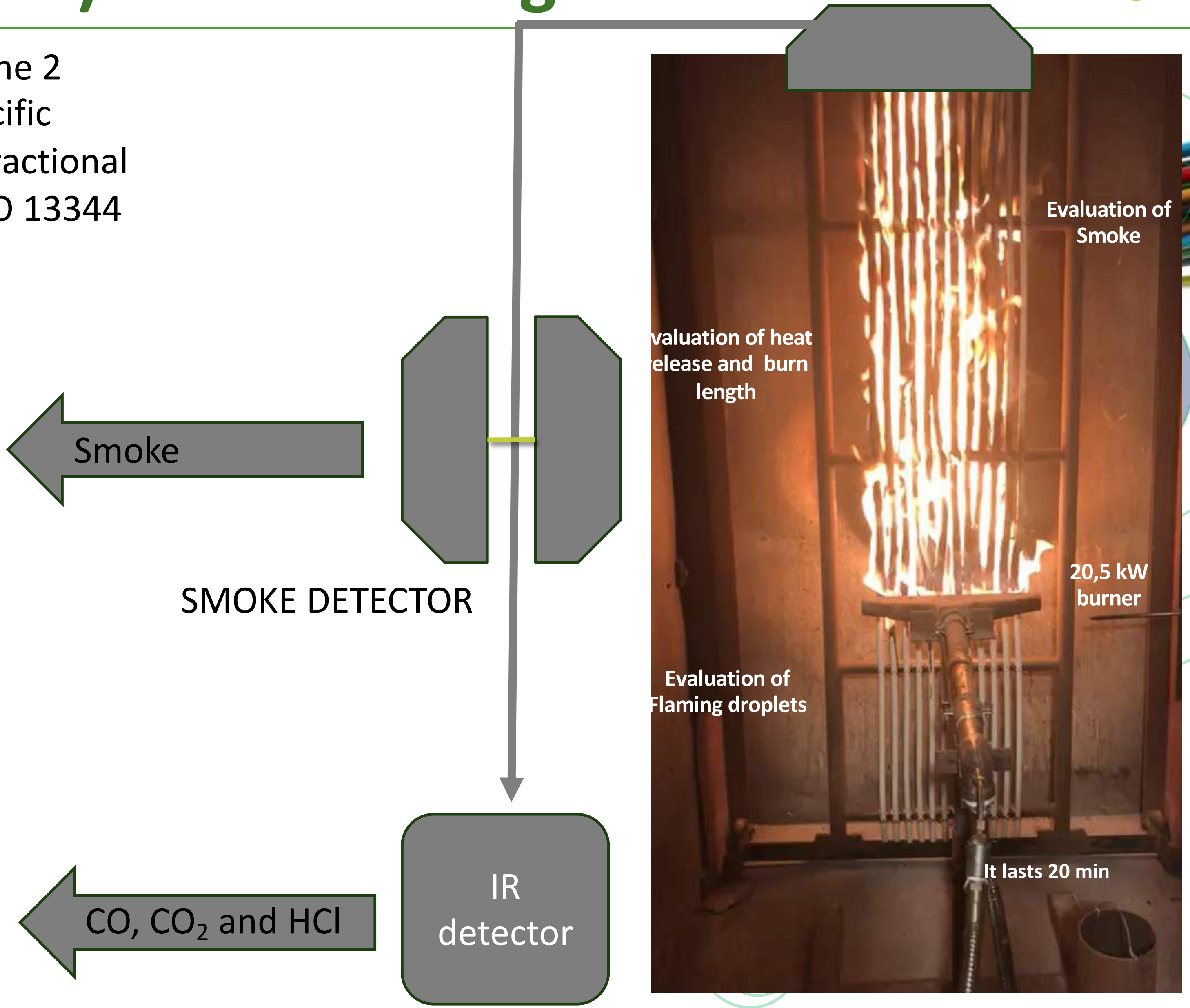
Table 15.2

4 LSA Cables n1 (2024): EN 50399 + gas detectors

Ref. 33. evaluated also the classification of the 2 cables according to EN 50399 and using specific sensors for CO, CO_2 and HCl even the FED (fractional exposure dose) according to according to ISO 13344







Picture 16: EN 50399 performed on FG16OR16 cable

4 LSA Cables n1 (2024): EN 50399 + gas detectors

PVC4CABLES

Ref. 33. evaluated also the classification of the 2 cables according to EN 50399 and using specific sensors for CO, CO2 and HCl even the FED (fractional exposure dose) according to according to ISO 13344

Measurement	"Zero halogen" Polythene – based cable FG16OM16 5G 1,5 mm² (Laboratory reference no. 900/24)	PVC – based cable FG16OR16 5G 1,5 mm² (Laboratory reference no. 901/24)
Flame spread FS (m)	2.25	0.85
Total heat release $THR_{1200\,s}$ (MJ)	16.2	7.01
Peak of heat release rate Peak HRR (kW)	58	25
Fire growth rate index (max) Figra (W/s)	220	143
Peak of smoke release rate SPR (m^2/s)	0.05	0.28
Total smoke released TSP 1200 s (m^2)	15	82
Flaming droplets	None	None
Class according to EN 13501-6	Dca, s1-d0	B2ca, s2-d0

Table 17.1

Table 17.1. shows the classification parameters. FG16RO16 LSA is much more performant than FG16OM16

	"Zero halogen" Polythene – based cable FG16OM16 5G 1,5 mm² (Laboratory reference no. 900/24)	PVC – based cable FG16OR16 5G 1,5 mm² (Laboratory reference no. 901/24)
CO_2	3500 g	2890
CO	408 g	388
HCl	N/A	10 g
FED	0.81	0.77

Table 17.2

Table 17.2. shows the FED. PVC cable ha a lower value due to the fact that it burns less.

4 LSA Cables n2 (2022): : EN 50399 + gas detectors

Ref 34, performing EN 50399, highlighted that the measure of CO production from low smoke acidity cable decays in time (yellow curve, Figure 18.1), while CO HFFR increases (green curve, Figure 18,1). CO particularly drops because it is linked to HCl concentration in the gas phase. (equation 1)

$CO + OH \rightarrow CO_2 + H$ (1)

In absence of HCl this reaction can happen. When HCl decays CO decays. The cumulative production of CO LSA compounds is therefore much less comparing to standard PVC compound for cables even better than the best HFFR. (Figure 18,2)

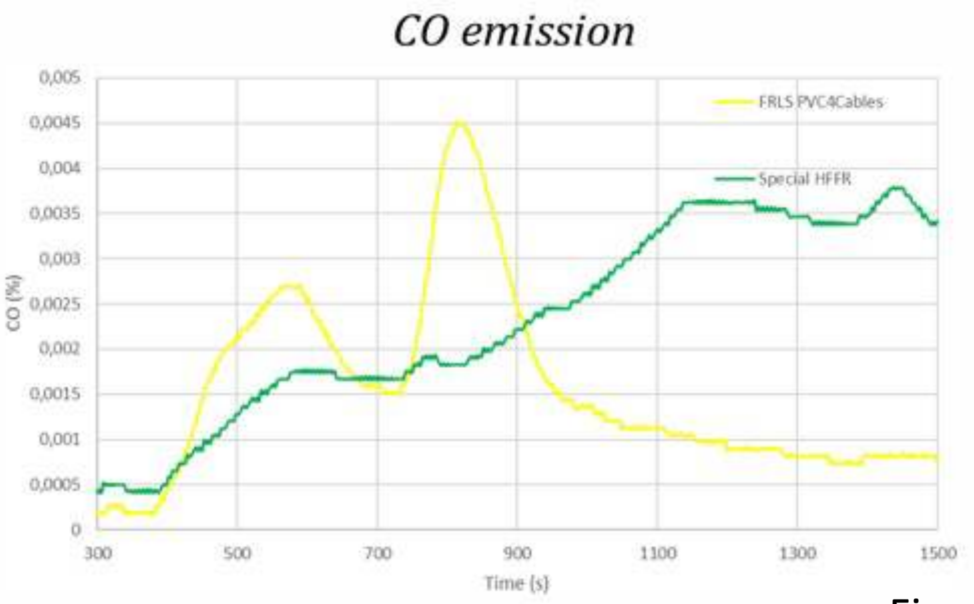


Figure 18,1

FR(LS) PVC vs HFFR compounds: total CO Production evolution

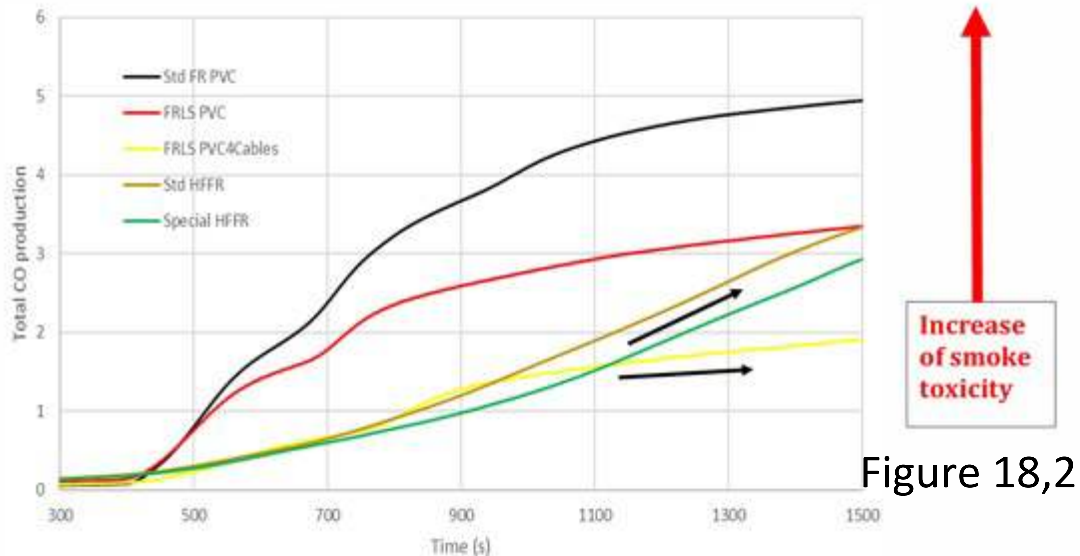


Figure 18,2

4 New LSA Cables: real fire scenario n. 1

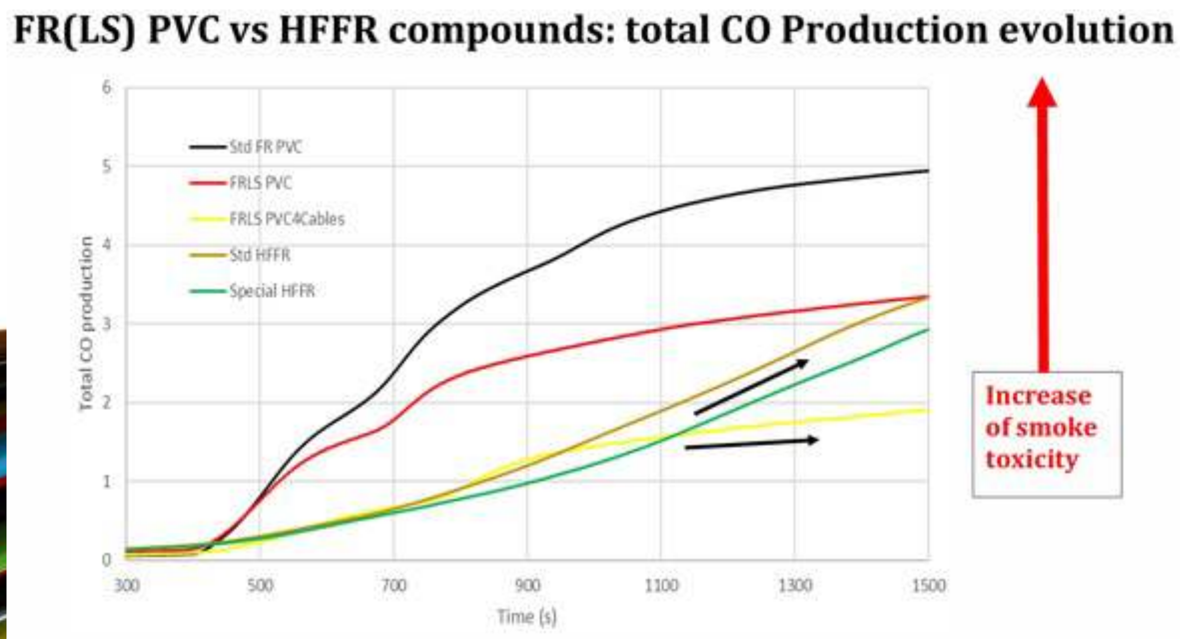
Fire Scenario number 1: A room goes in flashover, people die for:

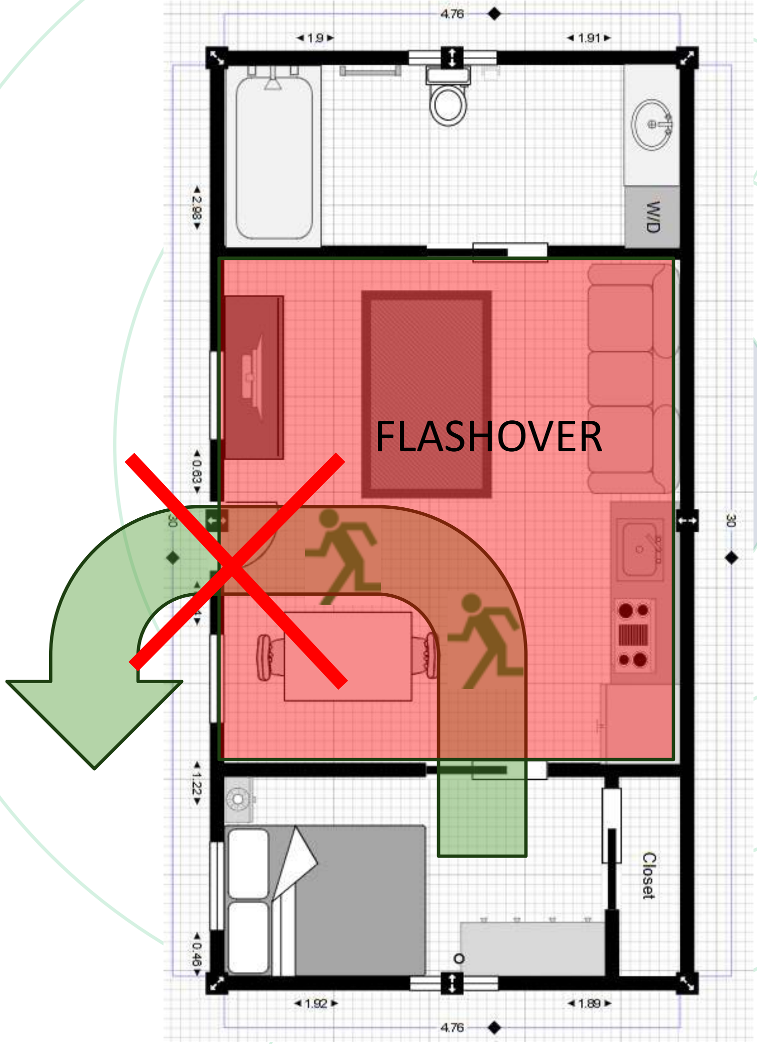
CO monoxide

Hot air (> 80 °C)

Heat

Collapse of the structure

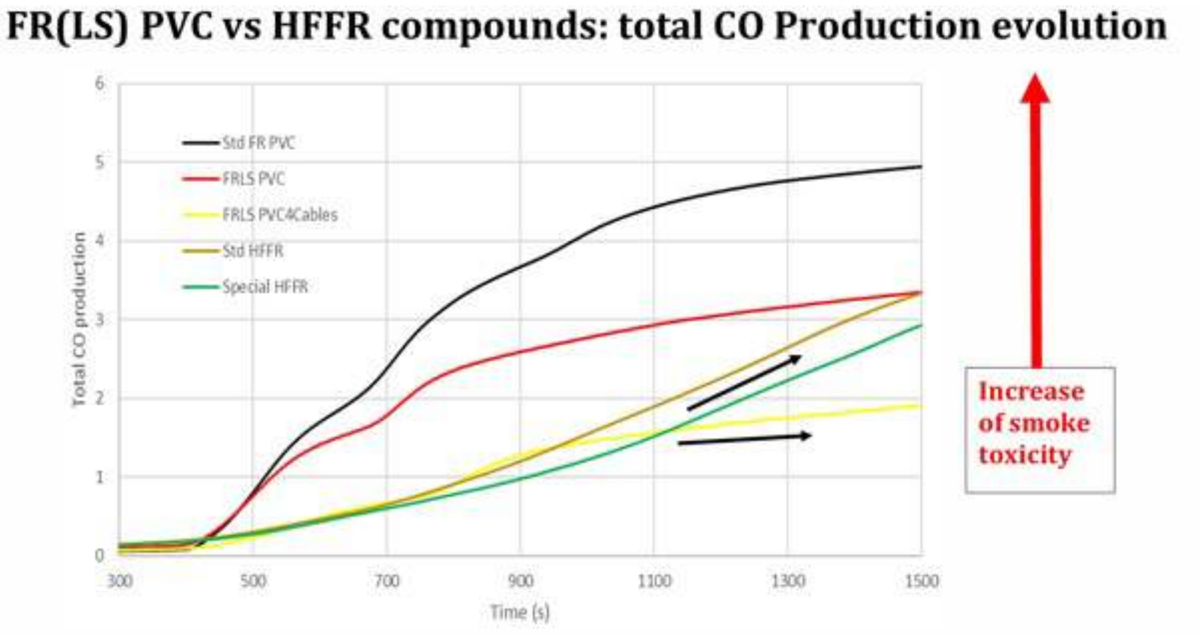




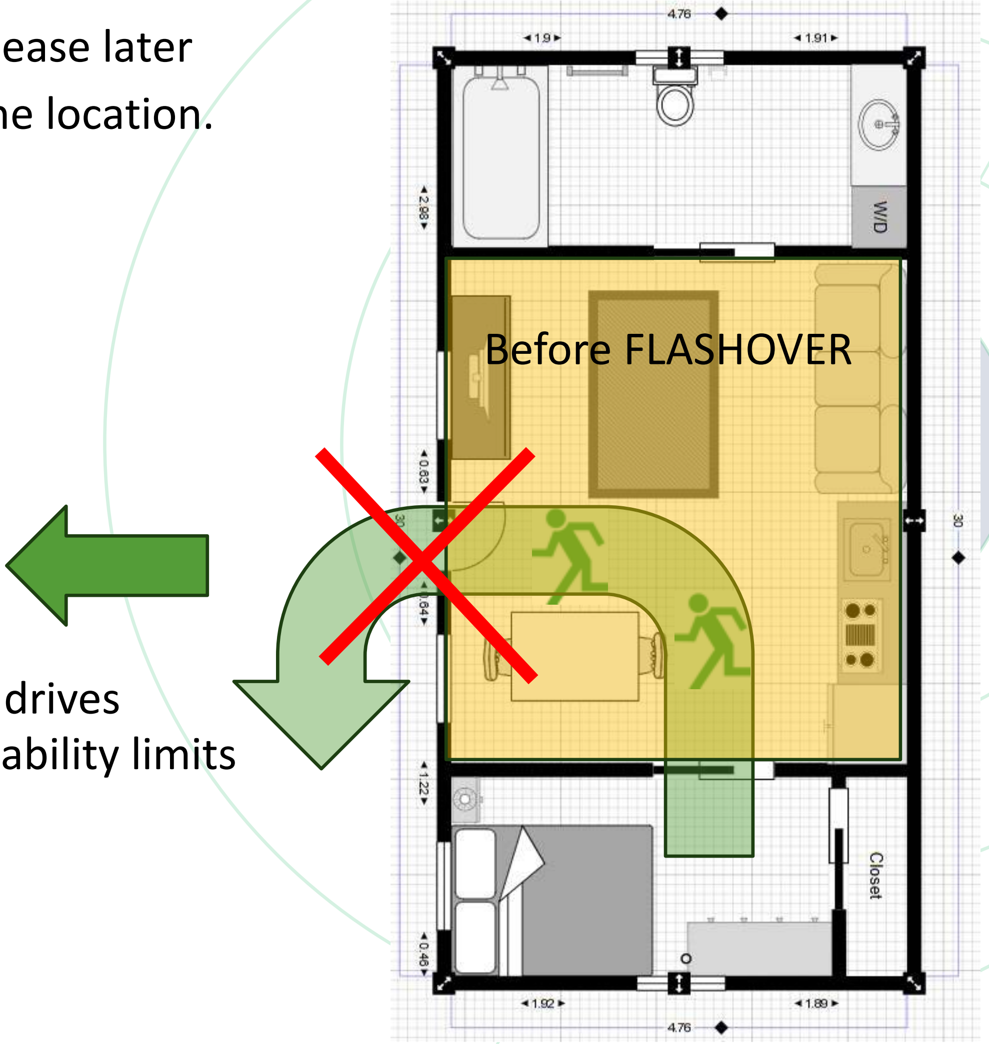
4 New LSA Cables: real fire scenario n. 4/5

Fire Scenario number 4 and 5: A room goes in flashover, and people die for:

CO monoxide is the dominant intoxicant, HCl decays and it is release later because PVC article burn later than the common furnishing in the location.

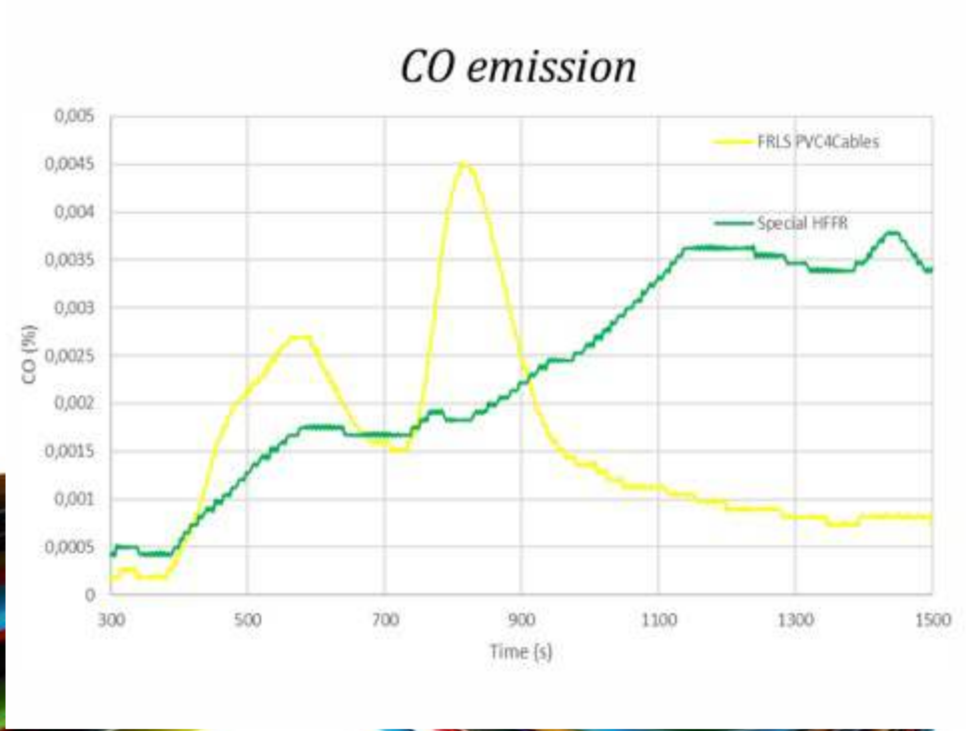


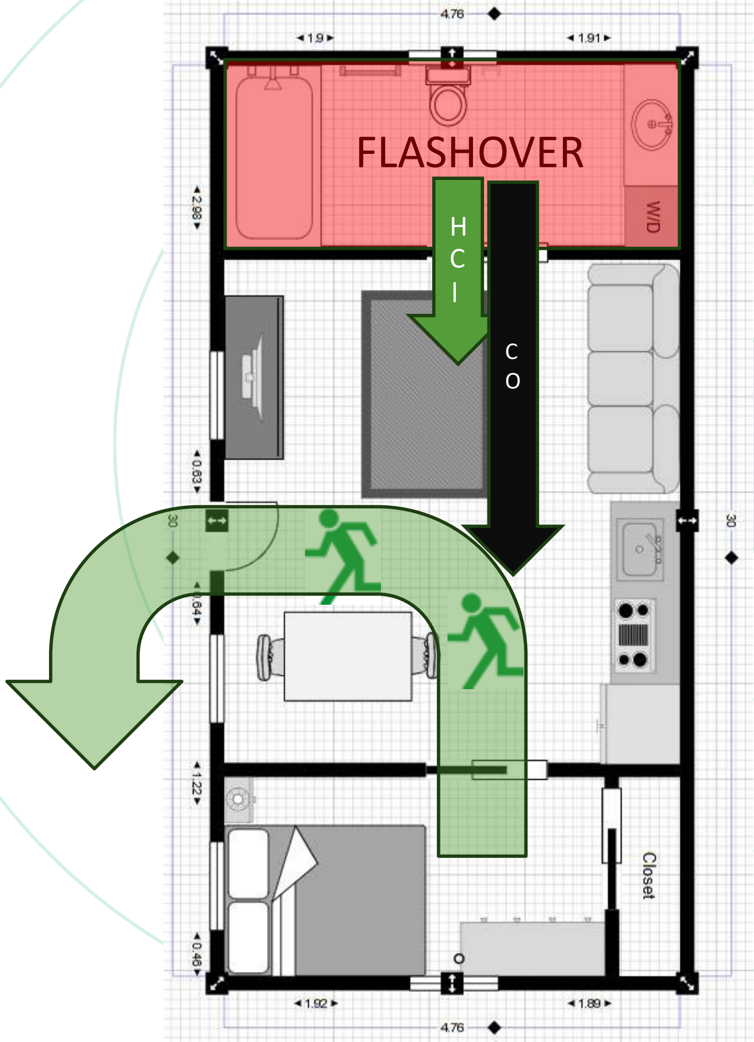
CO drives tenability limits



4 New LSA Cables: real fire scenario n. 6

Fire Scenario number 6: A room goes in flashover, HCl is released (Acid scavengers do not work), HCl decays, CO from PVC is less than HFFR and does not travel far from the location where it originated. CO is released in the same amount after the flashover from every polymer (20% of their mass)





5 Conclusions

1) Toxicity of the effluents is mainly related to CO, and acidity assessment has no correlation with toxicity
2) Small scale tests that evaluating toxicity are not representative of real fire scenarios
3) The use of EN 50399 with sensors for CO, CO_2 and HCl confirmed that it can be a powerful method for assessing the effluent toxicity in combination with ISO 13344 through FED
4) LSA cables showed higher toxicity potential in small scale and lower in medium scale (FED 0,77 vs. 0,81)
5) The EN 50399 + sensors must be repeated for the third time to confirm definitely the data
6) In real fire scenarios HCl decays and the HCl quantity in the gas phase could be even less
7) Large scale tests are suggested for assessing if HCl is a real concern in the fire safety

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6 References

[(PDF) Full paper is available here)]

7 About us

PVC Forum Italia (www.pvcforum.it) is the Italian association that brings together the leading companies in the production, compounding, and processing of PVC, as well as manufacturers of additives and processing machinery. Based in Milan, PVC Forum is part of the European network of PVC forums connected to ECVM (European Council of Vinyl Manufacturers), the European association of PVC producers, which is a division of the association of European plastics producers (PlasticsEurope).

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VinylPlus® is the Voluntary Commitment to the sustainable development of the European PVC industry. The program was developed through an open dialogue with stakeholders, involving industry, NGOs, legislators, representatives of civil society, and end-users of PVC. VinylPlus® operates in the 27 European Union countries plus Norway, Switzerland, and the UK. VinylPlus® is registered as a SMART partnership on the UN's Partnerships for the SDGs platform.

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PVC4Cables is the ECVM platform dedicated to the PVC cable supply chain. It brings together PVC resin producers, stabilizer and plasticizer manufacturers, and PVC compounders. It is open to the participation of PVC cable manufacturers, recyclers, and industry associations. PVC4Cables aims to be a driver for environmentally compatible innovations in the PVC cable sector and to serve as a point of reference for dialogue and communication with all stakeholders: cable manufacturers, legislators, designers, installers, electricians, media, and the general public.

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Thank you for your attention

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